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Electrospun Sodium Titanate Fibers for Fast and Selective Water Purification

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† This paper is dedicated to the memory of our wonderful colleague, Professor Risto Harjula, who passed away September 11, 2017.

Electrospun Sodium Titanate Fibers for Fast and Selective Water Purification

From the environmental and end-users viewpoints, electrospun ion exchange fibers provide highly efficient and sustainable material for separation of for example trace pollutants, such as radionuclides and heavy metals. This work aimed to reduce the amount of ion exchange material needed per unit volume of raw material subjected to an ion exchange process. We present a very simple process to electrospinning of sodium titanate fibers, but also test results of ion exchange kinetics measurements. Sodium titanate fibers are very promising material and it is possible that by exploiting electrospun inorganic submicron fibers the ion exchanger mass required for a given capacity can be decreased significantly.

Keywords: inorganic ion exchange; ion exchange; electrospinning; sodium titanate; water purification

Introduction

Inorganic ion exchangers have demonstrated their usability in large-scale commercial applications where the concentration of the target element is extremely low compared to total element concentration [1]. This is the result of the high ion-exchange selectivity of these materials [2-5]. Inorganic ion exchange materials are used in ton scale for separation of radionuclides in Fukushima nuclear accident site (Advanced Liquid Processing System, ALPS™), for example [6].

Sodium titanate is one widely exploited inorganic ion exchange material [4-8]. Although sodium titanates are generally considered as typical weakly acidic ion exchangers [4, 9], some debate on the exact sorption mechanism still remains. Merceille *et al* have reported that sorption mechanism has to be described by two models: the reaction kinetic model and the diffusion model [10]. They concluded from their kinetic experiments that the ion exchange is due to the chemisorption and not due to the physisorption. And second, the ion exchange involves many diffusion-controlled steps, but boundary-layer diffusion and intra-particle diffusion are the most limiting diffusion processes.

Typically, the kinetics of ion exchange and inorganic ion exchange materials, in particular, have been considered slow. The main reason for this is the physical constrains of the materials that are used in granulated form. With typical inorganic ion exchange materials, the ion exchange sites are mostly inside a tunneled and ridged structure that hinders the flow and exchange of ions inside the material. This feature decreases the throughput of the process and the interest to the technique in many cases. Our approach here was to decrease the length that ions have to diffuse into the material by preparing the ion exchange material in submicron fiber form. Typically decreasing

the particle size would lead into a pressure build up and clogging of the ion exchange column. Instead, preparing the material in the form of nonwoven fiber mat with high surface area to volume ratio is considered ideal, because the netlike macrostructure resists close packing and consequent clogging of the column. Because of the small diameter of the fibers, all ion exchange sites are within small diffusion length from the fiber surface, which enhances the kinetics as compared to conventional ion exchange materials.

There are several methods to prepare submicron fibers, but only a few techniques to prepare inorganic fibers. The most common, straightforward and up-scalable method is electrospinning [11, 12]. Electrospinning is a method that can easily produce macroscopic amounts of fibers from several materials like polymers and metal oxides. In an electrospinning process, a polymer solution is fed to a metallic needle that is connected to a high voltage power source. The electric charge causes an eruption of a polymeric jet from the polymer droplet at the needle tip. During a flight from the needle to the grounded collector, the jet elongates, dries, and is finally collected as solid fibers. To prepare inorganic oxide fibers, the electrospinning solution has to contain also a proper amount of metal precursors, for example titanium isoproxide and sodium acetate. After electrospinning, the collected fibers are calcined, typically in air atmosphere. During calcination polymer is combusted and metal precursors are oxidized to metal oxides, like TiO_2 [13]. Crystallinity of the final product depends on calcination temperature and time.

In this study, we present a novel approach for improving the efficiency and sustainability of ion exchangers, more specifically sodium titanate, in the form of sub-micron fibers. Our particular aim is to reduce the amount of ion exchange material needed per unit volume of raw material subjected to an ion exchange process. The use

of submicron fibers provides considerable advantages. Fibers are easier to handle and keep fixed than powders that typically need to be bound to a separate support material. Fibrous materials form self-supporting and liquid-permeable structures within housings of different kinds. It may be estimated that by exploiting electrospun inorganic submicron fibers the ion exchanger mass required for a given capacity can be decreased 10-fold, or maybe even up to 100-fold compared with the current granular ion exchange materials. From the environmental and end-users viewpoints, the electrospun ion exchange fibers provide a highly efficient and sustainable material for separation of for example trace pollutants, such as radionuclides and heavy metals.

Experimental

Chemicals and materials

The precursor solutions for electrospinning were made by preparing first 7 wt% PVP (polyvinyl pyrrolidone, Mw 1300 000 g mol^{-1}, Alfa Aesar) solution with absolute ethanol (EtOH) as a solvent. A metal precursor solution was made by mixing 6 ml of 1:1 volume ratio glacial acetic acid and ethanol (HAc/EtOH), 1.50 ml titanium tetraisopropoxide and 0.2664 g sodium acetate so that the Ti/Na molar ratio was 1.55. After 30 min stirring the polymer solution and metal precursor solution were mixed together by adding 7.5 ml of 7 wt% PVP/EtOH solution to the just made metal precursor solution. This solution is ready for electrospinning after 1 h stirring.

Fiber preparation

Fiber formation was done by a self-made electrospinning apparatus that consists of a high voltage supply (Gamma High Voltage Research Inc. ES30P — 5 W/DDPM), a 6 inches silicon wafer as a fiber collector, a plastic syringe, a 22 G blunt stainless steel

needle as a spinneret, and a syringe pump (KD Scientific KDS-230). The whole electrospinning setup was assembled in a fume hood. In a typical procedure, the polymer solution that contains the metal precursors was placed into the plastic syringe. Using the syringe pump, the precursor solution was delivered to the stainless steel needle at a constant flow rate of 1.000 ml/h. The needle was connected to the high voltage supply. The distance from the needle tip to the collector was set to 15 cm. Fibers were ejected from the needle tip when a high voltage of 15 kV was applied. The collected fibers were annealed at 500 °C for 4 h in air. During the calcination, organic parts of the fibers were removed and metal precursors were oxidized to metal oxides.

Analytical methods

The fibers were examined by field-emission scanning electron microscopy (FESEM, Hitachi S4800) and X-ray diffraction (XRD, PANalytical X'Pert PRO equipped with a Cu Kα source, $\lambda = 1.5405$ Å). The thermal combustion of the sodium titanate–PVP composite fibers during calcination was studied with dynamic thermogravimetric analyses (Mettler Toledo Star System with a TGA 850 Thermobalance). Samples were heated in open alumina pans from 25 to 800 °C with a heating rate of 10 °C/min under airflow of 50 ml/min. The specific surface area and pore sizes were measured with BET analysis (Micromeritics ASAP2020 Gas sorption analyzer).

Ion exchange experiments

Ion exchange properties of the materials were studied by measuring their metal uptake properties using batch experiments. In these experiments, 10 mg of finely ground material was placed in a polyethylene vial with 10 ml of test solution. Samples were equilibrated for one day in a constant rotary mixer, in which time the solid/solution system reached an equilibrium. The solid phase was then separated by centrifuging (3

000 g) the vials for 10 minutes and 5 ml subsamples were pipetted and filtered with a 0.2 μm filter (PVDF I.C. Arcodisc, Gellman Sciences) for concentration measurements. The equilibrium pH was measured from the remaining solution.

The results from these batch experiments are presented here as distribution coefficients (K_d, ml/g) that reveal how the element of interest is distributed between the initial sample solution and the solid material after one day equilibration time. K_d was calculated as follows:

$$K_d = \frac{(c_i - c_{eq})}{c_{eq}} * \frac{V}{m} \qquad (1)$$

Where c_i = initial metal concentration of the solution, c_{eq} = metal concentration of the solution at equilibrium, V = volume of the solution, and m = mass of the solid material.

In the kinetic experiment 60 mg of hydrogen form ion exchange material was mixed with a magnetic stirrer with 60 ml of 0.1 M $NaNO_3$ solution, traced with Sr-85, in a beaker glass from which samples were taken as a function of time (2, 5, 10, 15, 30, 60, 180, 1200 min). The samples were then phase separated as stated above and their Sr-85 activity was measured. The effect of pH on the metal uptake was measured in 0.1 M $NaNO_3$ solution traced with Sr-85 or Co-57. The concentration of the radiotracers was below 10^{-9} M in the test solutions. The gamma activities of the radiotracers were measured using 3" Na(I) scintillation detector (Wallac Wizard 3" Na(I) gamma-analyzer).

Results and discussion

Preparation and Characterization of sodium titanate fibers

Sodium titanate fibers were prepared successfully by electrospinning solution that contained polyvinyl pyrrolidone (PVP), ethanol, acetic acid, titanium(IV)isopropoxide and sodium acetate. Titanium isopropoxide was hydrolyzed during the electrospinning process [14], and therefore the fibers had amorphous titanium dioxide already before the calcination. The electrospinning process was followed by calcination in air at 500 °C for 4 hours. The calcination temperature was selected on the basis of the TGA measurement, Figure 1.

[Figure 1. near here]

Figure 1 shows thermogravimetric curves of the as-electrospun sodium titanate – PVP composite fibers and bare PVP fibers. The TG curves show in both cases a small initial mass decrease below 100 °C, most likely due to evaporation of residual ethanol and acetic acid as well as adsorbed humidity. Otherwise the TG curve of the bare PVP is similar to that Peniche et al. [15] reported in their study. In the temperature range 300 - 400 °C a step is observed in the PVP curve as the polymer begins to degrade by releasing side substituents, like pyrrolidones. In this temperature range pyrrolidone is volatile and easily combusted. Above 400 °C the weight lost is due to the combustion of polyene sequences until the residue at 700 °C is about 0.3 %.

As compared to the PVP fibers, the sodium titanate - PVP composite fibers have same kind of trends in the TG curve, but shifted to lower temperatures. The temperature range between 200 and 250 °C shows the removal of the the pyrrolidone substituents. The deepest step in the TG curve at about 300 °C is due to the combustion of polymeric

chain. The temperature range between 300 and 450 °C shows slow removal of the remaining carbon and decomposition of sodium acetate. The shift of the PVP combustion to the lower temperatures must be due to the presence of sodium acetate and titanium dioxide. When reaching 500 °C the mass decrease is essentially over and the residue is about 30 %. These results verify that calcination at 500 °C for 4 hours in air should be appropriate for removing the PVP and turn the product into sodium titanate.

FESEM images show that the average diameter of the calcined electrospun fibers was about 200 nm, Figure 2. The fibers exhibit smooth surfaces. XRD verified that the fibers were crystalline, Figure 3. The fibers were mainly a mixture of titanium dioxide (TiO_2) and monoclinic sodium titanate ($Na_2Ti_6O_{13}$), but also minor peaks of hexagonal sodium peroxide (Na_2O_2) and tetragonal sodium titanate monohydrate ($Na_2TiO_4 \cdot H_2O$) were found.

[Figure 2. near here]

[Figure 3. near here]

For comparison, commercial sodium titanate ion exchange material, SrTreat® powder (Fortum Corporation) was also characterized. SrTreat® is produced by a wet chemical process, boiling granular TiO_2 in NaOH [16]. Figure 4 shows FESEM images of SrTreat®. The granules of SrTreat® are comprised of agglomerated, 1 µm particles and the particle surfaces seem to be porous. The broad peaks in the XRD pattern in Figure 5 show that particles are mostly nanocrystalline or amorphous. Based on the XRD the material consists of several phases like cubic Na_2TiO_3, tetragonal $Na_2TiO_4 \cdot H_2O$. There are also strong reflections from monoclinic Trona, that is also known as natural soda, $Na_3H(CO_3)_2 \cdot 2H_2O$. Trona is most probably an impurity in technical grade of NaOH.

[Figure 4. near here]

[Figure 5. near here]

Specific surface area and pore size of the materials were analyzed with BET analysis, **Error! Reference source not found.**. The specific surface areas were very similar for the fibers and SrTreat®. BET surface area of the electrospun sodium titanate fibers was 7.0 m^2/g and that of SrTreat® 7.1 m^2/g. The most significant difference between the electrospun fibers and SrTreat® is in the pore size. Pore size of the electrospun fibers is only ~ 109 Å, compared to SrTreat® with a pore size of almost double ~200 Å. Furthermore, even if the specific surface areas are nearly the same, the surfaces are clearly differently exposed as seen in SEM images. The fibers are dense and hence the measured surface comes mostly from their outer surface that will be in intimate contact with the solution to be treated. By contrast, a major part of the surface measured for SrTreat® is inside the porous particles. To access these ion exchange sites the ions in the solution need to diffuse into the porous particles.

Ion exchange properties

The synthesized sodium titanate fibers showed good strontium uptake properties. The distribution coefficients (K_d, ml/g) measured for the sub-micron fiber material were at a level comparable with earlier results of granular material [3, 17] and showed high affinity of the material to strontium ions over other competing ions, such as sodium (Figure 6). In the earlier studies, the granular sodium titanate showed high selectivity towards strontium ions and it is used for selective strontium separations in large-scale industrial operations, for example in Fukushima Daichii nuclear power site [6]. The fibrous material shows also similar cobalt uptake trend as for strontium. This is somewhat different compared to the granular material that doesn't show high cobalt uptake after alkaline synthesis procedure. However, hydrogen form titanates are known

for their good cobalt uptake properties [18]. The curvature in cobalt uptake trend at pH 9 can be explained by the formation of $Co(OH)_2$ that, as a neutral species, was not taken up by the material.

[Figure 6. near here]

The ion exchange kinetics of ridged, inorganic materials has been one of their major drawbacks. Our approach was to decrease the particle size of the material into sub-micron scale in two directions (x- and y-directions) by making the materials in fibrous form (macroscopic in z-direction). The kinetic ion exchange experiments showed that at the first two experiment points the granular materials with higher surface area and porous structure showed slightly higher strontium uptake but after 10 minutes the fibrous material had higher distribution coefficients (Figure 7). The fibrous material did not show a change of the uptake trend while the uptake trend of the granular materials was clearly bent suggesting hindered strontium uptake, most probably due to the longer diffusion lengths into the tunneled structure of the granular material.

[Figure 7. near here]

Conclusions

The results described in this paper show that inorganic sodium titanate fibers can be prepared by electrospinning. The produced fibers have sub-micron scale diameter that ensures relatively short diffusion lengths of the exchanging ions to the ion exchange sites inside the material, i.e. fast ion exchange kinetics. The fibers form large, net-like structures that restrain clogging of the material and enable good flow-through properties in column mode ion exchange processes. Fibers have metal (Sr) uptake properties comparable to commercial, granular sodium titanate ion exchange material SrTreat®. The sodium titanate fibers are very promising ion exchange materials and it is possible that by exploiting electrospun inorganic submicron fibers the ion exchanger mass

required for a given capacity can be decreased significantly.

Acknowledgments

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Figure 1

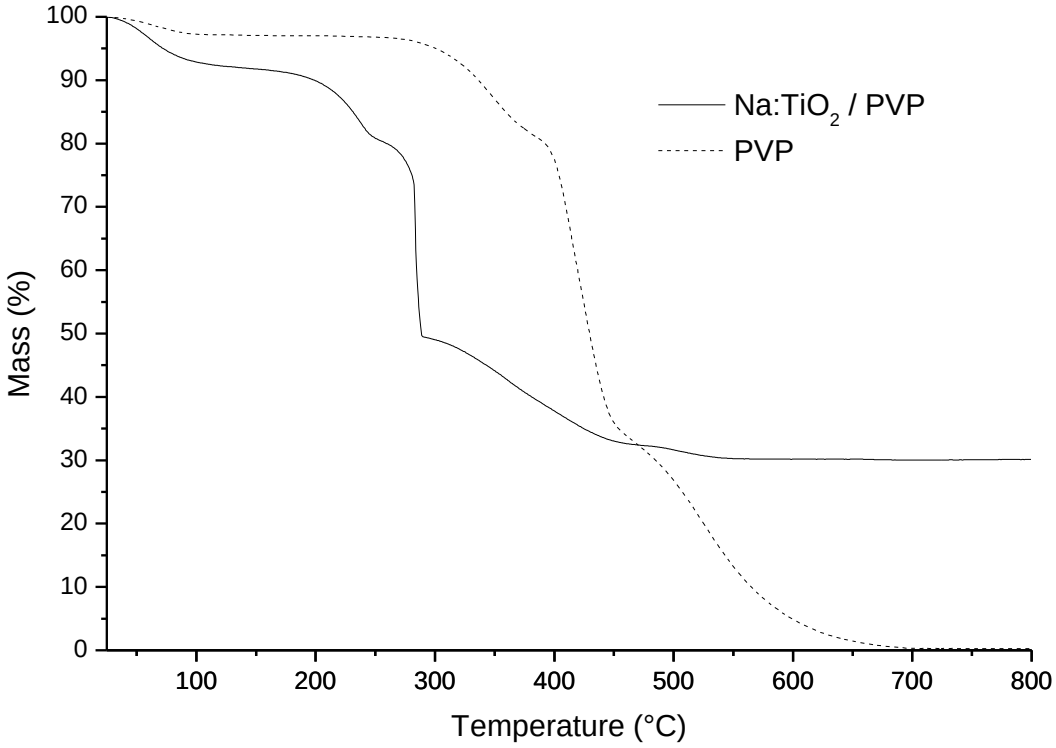
Na:TiO2 / PVP
PVP
Mass (%)
Temperature (°C)
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
600
700
800

Figure 2

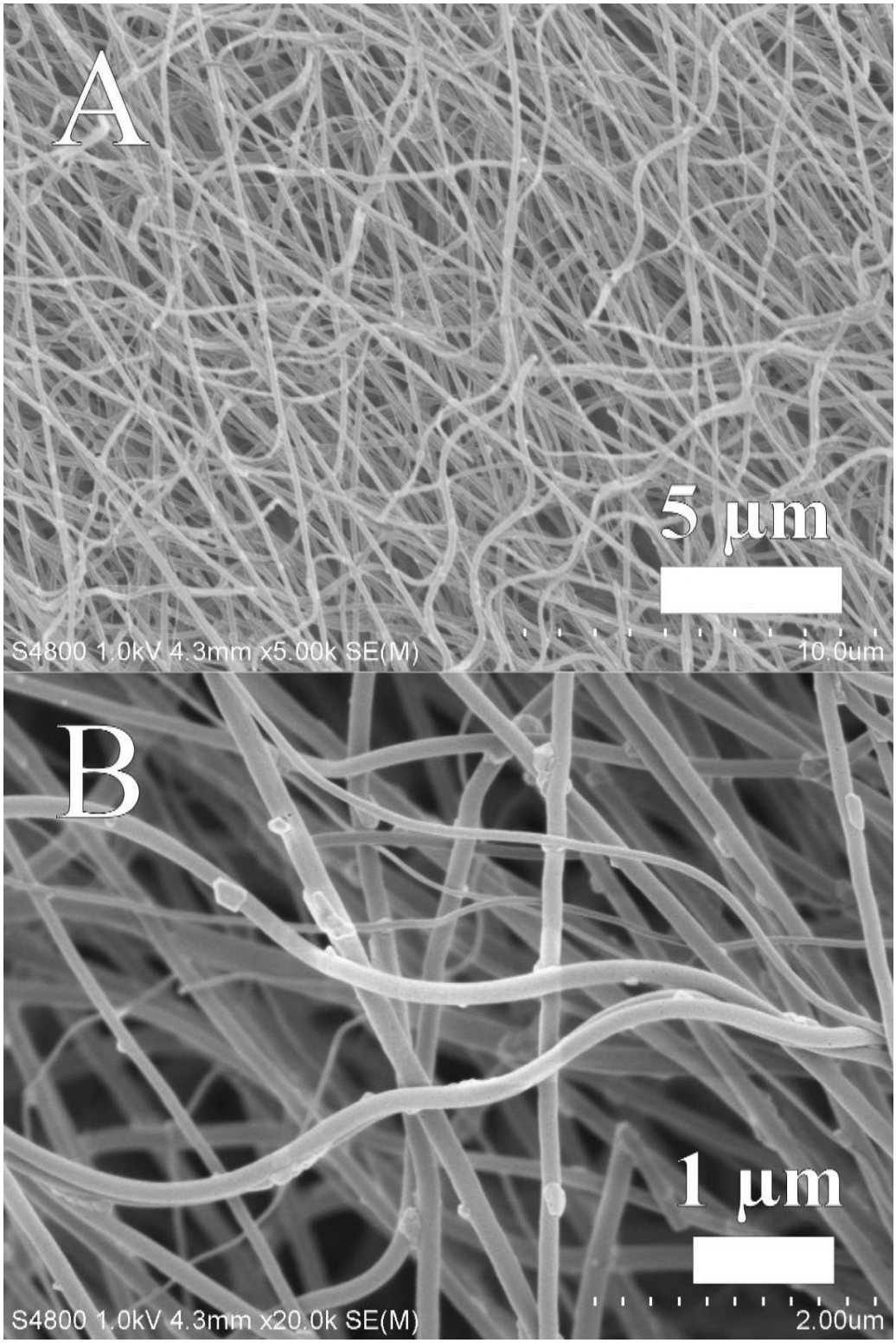
A
5 µm
S4800 1.0kV 4.3mm x5.00k SE(M)
10.0um
B
1 µm
S4800 1.0kV 4.3mm x20.0k SE(M)
2.00um

Figure 3

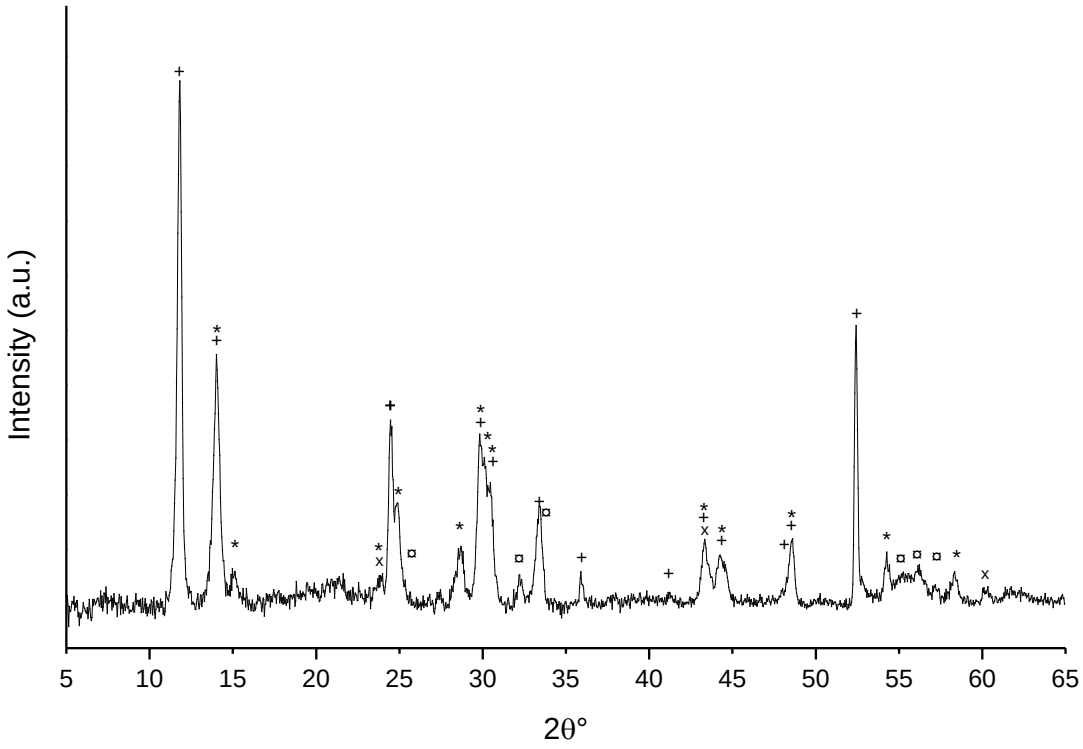

Figure 4

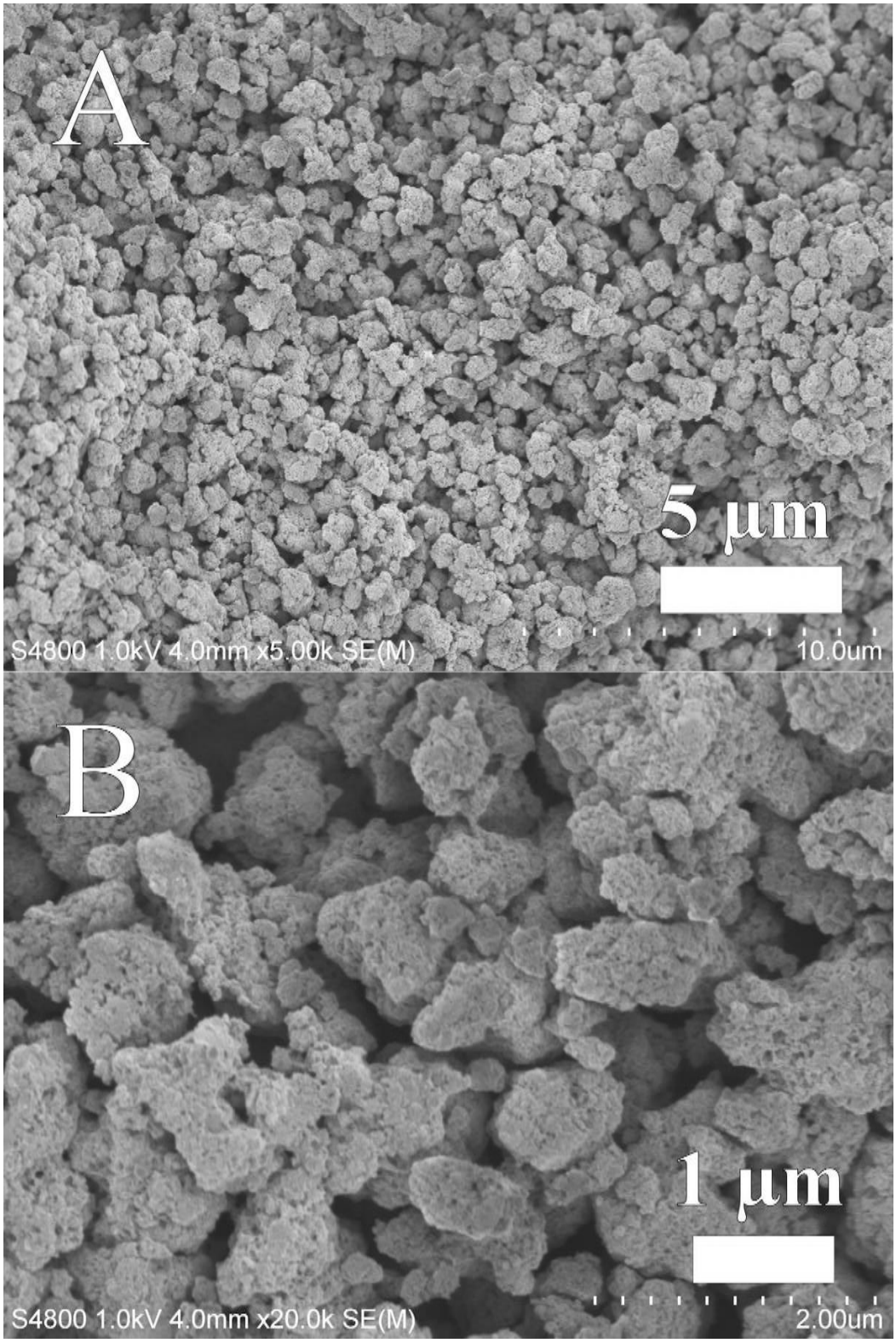
A
5 µm
S4800 1.0kV 4.0mm x5.00k SE(M)
10.0um
B
1 µm
S4800 1.0kV 4.0mm x20.0k SE(M)
2.00um

Figure 5

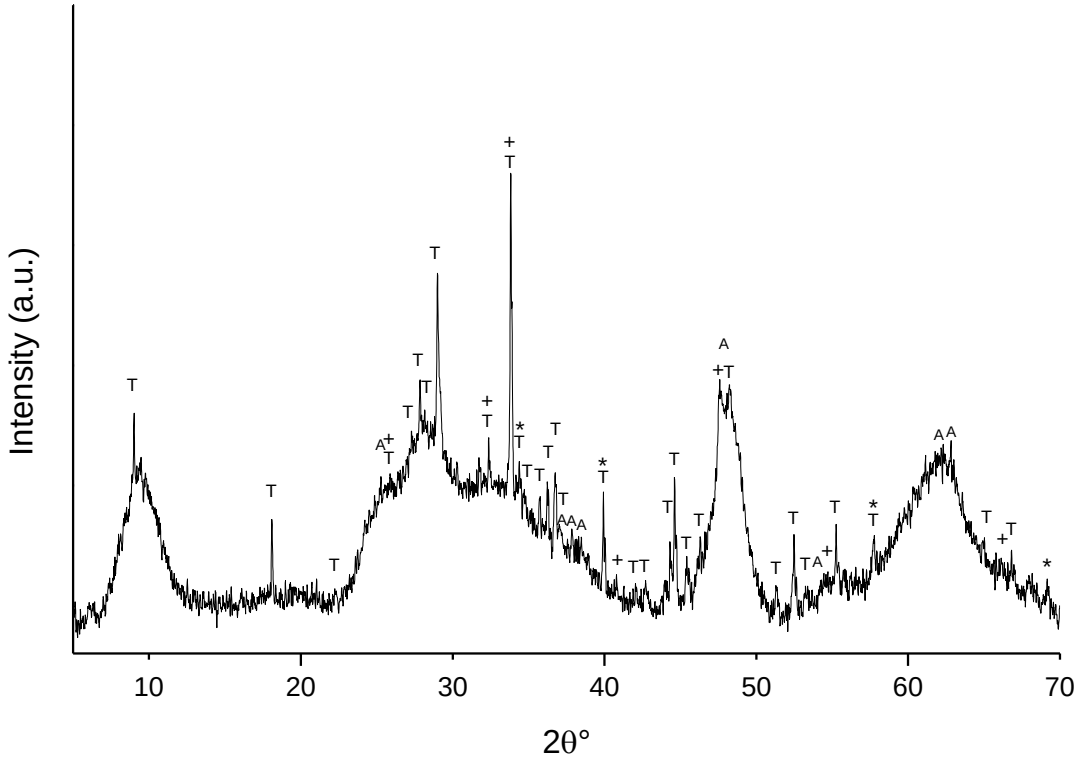

Figure 6

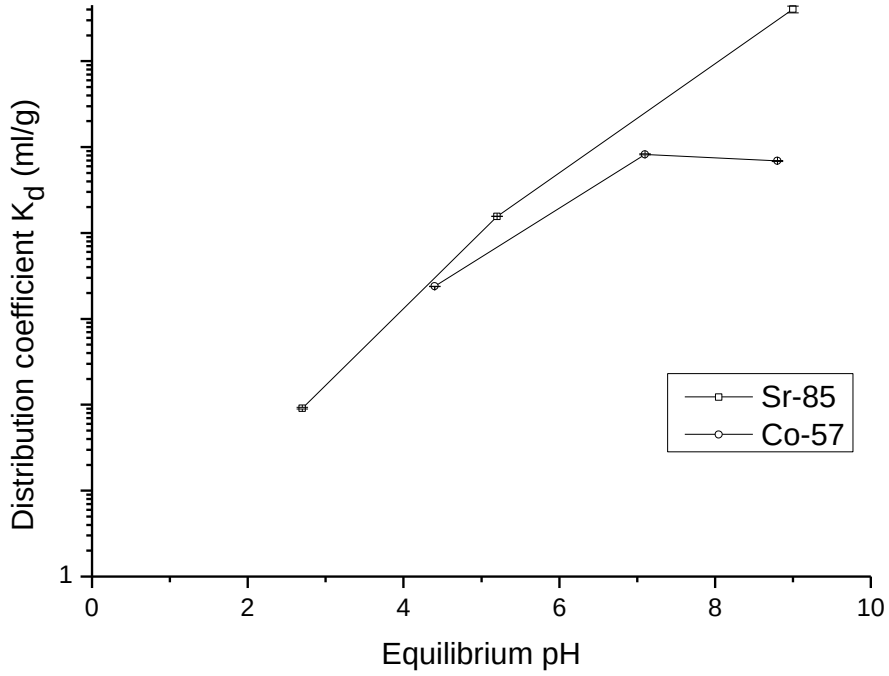
Distribution coefficient K_d (ml/g)
1
0
2
4
6
8
10
Equilibrium pH
Sr-85
Co-57

Figure 7

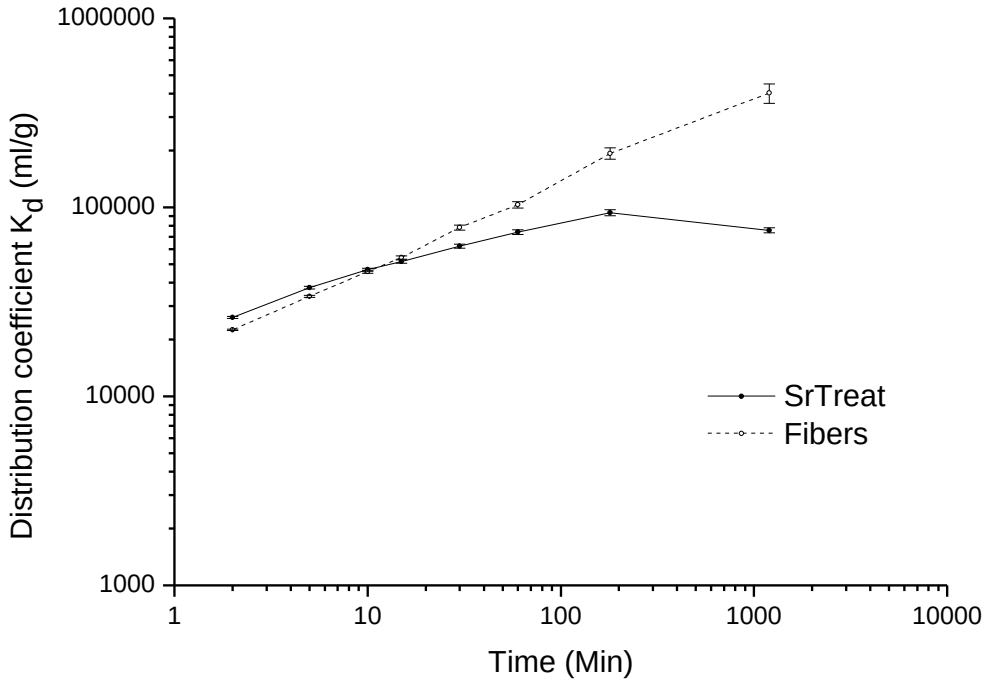
1000000
100000
10000
1000
Distribution coefficient K_d (ml/g)
1
10
100
1000
10000
Time (Min)
SrTreat
Fibers

Figure 1. TGA measurement of the as-electrospun sodium titanate - PVP composite fibers (solid line) and for comparison as-electrospun PVP fibers (dashed line) heated at 10 °C/min under air.

Figure 2. FESEM images of calcined electrospun sodium titanate fibers with different magnifications.

Figure 3. XRD pattern of electrospun sodium titanate fibers after calcination. The symbols refer to TiO_2 (*), $Na_2Ti_6O_{13}$ (+), $Na_2TiO_4 \cdot H_2O$ (¤) and Na_2O_2 (x)

Figure 4. FESEM-image of granular SrTreat® ion exchange material with different magnifications.

Figure 5. XRD pattern of commercial sodium titanate, SrTreat® powder. The symbols refer to Trona, $Na_3H(CO_3)_2 \cdot 2H_2O$ (T), Na_2TiO_3 (*), $Na_2TiO_4 \cdot H_2O$ (+) and anatase (A).

Figure 6. Distribution coefficients of Sr-85 and Co-57 in 0.1 M $NaNO_3$ solution as a function of pH for electrospun sodium titanate fibers.

Figure 7. Distribution coefficient K_d (ml/g) of SrTreat® and calcined electrospun sodium titanate fibers as a function of shaking time (min). pH in measurements was 6.5.